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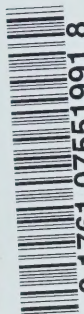
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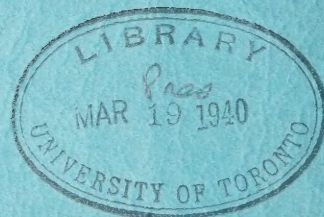


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CONCENTRATIONS OF WATER-SOLUBLE PRESERVATIVES
IN TREATED TIMBER

BY

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OTTAWA, CANADA
1939

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Concentrations of Water-Soluble Preservatives in Treated Timber

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Introduction

When wood is treated with water-soluble inorganic salts in order to preserve it against decay or insects, it has been found that movement of water in the wood effects changes in the distribution of the preservative. There is very little information available in the literature regarding the quantity of water-soluble salts remaining in treated timber after various periods of service or regarding the distribution of the salts immediately after treatment.

Under certain service conditions, as in a railway tie, the preservative is leached from the timber. Under other conditions, as in a round fence-post, there is also a movement of the water-soluble salts up the sapwood from the butt to the portion above the ground-line. Data obtained from examinations of ties and fence-posts after various periods of service are presented below in Sections A and B.

The upward movement of moisture in the sapwood of fence-posts has been utilized to treat green posts by standing the butts in a concentrated solution of copper sulphate. Data on the concentration of copper sulphate found in two fence-posts after treatment are presented in Section C.

A. Zinc Chloride Concentrations in Ties after 4
to 9 Years' Service

Materials Examined and History

Two jack pine ties, pressure-treated in 1924 with half a pound of zinc chloride per cubic foot, were placed in track in the vicinity of Lacombe, Alberta, in 1925, and removed in 1929.

Six Eastern hemlock ties, pressure-treated with half a pound of zinc chloride per cubic foot, were placed in track near Windsor Street Station, Montreal, Quebec, in 1929, and removed in 1938.

Examination

For the jack pine ties, analytical samples were prepared from one-inch cross-sections of the ties taken at intervals indicated in Table 1. Analyses were carried out by the standard ferrocyanide method. Table I shows the results in detail.

Table I

Zinc Chloride Concentrations in Jack Pine Ties
after 4 Years' Service

Distance of 1-in. Sections from end of Tie (Inches)	Lb. of Zinc chloride per cu. ft. calculated from zinc determinations	
	<u>Tie No. 1</u>	<u>Tie No. 2</u>
4 ¹ / ₂	0.126	0.139
8 ¹ / ₂	0.108	0.088
12 ¹ / ₂	0.104	0.069
24 ¹ / ₂	0.102	0.091
36 ¹ / ₂	<u>0.103</u>	<u>0.101</u>
Average (weighted) for entire tie	0.108	0.096

The Eastern hemlock ties were examined in somewhat greater detail than the jack pine ties. The six ties were sectioned longitudinally at right angles to the spike holes. One section of each tie was planed smooth and sprayed with potassium iodide-ferricyanide-starch indicator to secure data on penetration, and the set of six sections was photographed. Unfortunately, traces of iron in many parts of the ties reacted with the ferricyanide and obscured the characteristic zinc colour, and the test was of little value. The photograph is accordingly not reproduced.

Three of the ties -- Nos. 2, 4, and 5 -- were sectioned at points indicated in Table 2, and samples were analysed for both chlorine and zinc. Corresponding samples

from the top and bottom of the ties were analysed in each case. For tie No. 6 the average concentration of zinc chloride in pounds per cubic foot of wood was calculated.

Table 2

Zinc Chloride Concentrations in Eastern Hemlock Ties
After 9 Years' Service

Pounds of Zinc Chloride per cu.
ft. calculated from:

Tie No.	Size and Location of Section	Zinc Deter- minations		Chlorine De- terminations		Decay Rating of Section
		Top	Bottom	Top	Bottom	
2	10" Section, 16" from end	0.059	0.085	-	-	Advanced
4	10 $\frac{1}{2}$ " " , end	0.115	0.095	-	-	Sound
5	12" " , centre	0.138	0.065	-	-	Sound
6	3" Sections, average two ends	0.122	0.140	0.019	0.018	Slight
6	1" " , 7" from each end (av.)	0.104	0.093	0.015	0.015	Slight
6	10 $\frac{1}{2}$ " Section, under rail seat	0.055	0.067	0.014	0.009	Advanced
6	10 $\frac{1}{2}$ " " "rail seat	0.090	0.014	0.014	0.012	Moderate
6	2" Sections, 33" from each end (av.)	0.099	0.076	0.039	0.009	Sound
6	2" Section, centre	0.077	0.063	0.048	0.036	Sound
Average (weighted) for Tie No. 6		0.089	0.088	0.026	0.015	

The zinc chloride concentration in Tie No. 6, averaged over the entire tie, was 0.089 pound per cubic foot as calculated from zinc determinations and 0.021 pound per cubic foot as calculated from chlorine determinations.

Decay ratings of the spike holes were as follows:

Tie No.	1	Medium decay, both sets of holes
" "	2	Advanced decay, both sets of holes
" "	3	Advanced decay, and slight decay
" "	4	Moderate decay and slight decay
" "	5	Medium decay, both sets of holes
" "	6	Advanced decay and slight decay

Discussion

Examination of the analytical data shows, first, that in four years the concentration of zinc chloride, as calculated from zinc determinations, was reduced to about 20 per cent of its initial concentration in jack pine ties. In nine years it was reduced to a little less than 20 per cent in hemlock ties.

Variations throughout a single tie have little apparent significance; concentrations are somewhat higher at the ends; differences between top and bottom do not appear to have any special meaning.

The second important point to be noted is the great differences in Table 3 in concentrations of zinc chloride calculated from zinc determinations and from chlorine determinations. These differences are normally encountered in all similar work, and are due to the well-known property of zinc chloride of forming basic chlorides; zinc chloride and water react to form basic zinc chlorides (of variable composition with low solubilities) and hydrochloric acid. The hydrochloric acid is readily leached from the wood, and the net result is that the percentage loss of chloride originally present is greater than the percentage loss of zinc. It was noted more than seventy-five years ago that, when wood treated with zinc chloride is leached, the chloride is leached more rapidly than is the zinc ion. In a very interesting report (1) dated 1872, the following passage occurs; "I also notice the, at least, partial decomposition of the salt, the first portions of pure distilled water used for washing containing chlorine, but yielding no reaction for zinc." The subject has also been dealt with in detail by Bateman (2), who concluded from the results of analyses of ties taken from service that in the leaching of zinc chloride from wood the chlorine leaches faster than the zinc, part of which is left behind as an insoluble basic chloride. Bateman's figures are not strictly comparable with those given above, since they show concentrations at selected points in the treated shell only, while the latter are concentrations for the entire cross-sections of the ties.

Summary

Changes in concentration of zinc chloride in treated ties under service conditions are, first, a great reduction in the average concentration and, second, a greater reduction of chloride than of zinc concentrations.

In ties examined after various periods of service, it was found that the quantity of zinc chloride per cubic foot of wood remaining in various parts of individual ties varied considerably. In general, the decay was concentrated at and around the spike-holes and the ends, with little or no decay in the centre portion of the ties. It was not possible to draw any definite conclusions regarding the quantity of zinc chloride required to inhibit decay.

Owing to the time involved in carrying out the analytical work, it is not feasible, at present, to examine a sufficient number of ties to determine the rate at which the zinc chloride is lost in service or the amount required to inhibit decay. The indications are, however, that a considerable proportion of the loss occurs a few years after installation.

B. Zinc Chloride Concentrations in Butt-Treated Fence-posts

In 1931 a description was published of work ⁽³⁾ in which it was found that, after a year in the ground, a green spruce pole to the butt of which had been nailed a can containing dry zinc chloride contained a high percentage of zinc chloride at a point three feet above the ground-line, and comparatively little below the ground-line. The importance of this upward movement of a water-soluble preservative was recognized, and further work, as described below, was carried out.

Materials Examined and History

Three aspen poplar posts were butt-treated after seasoning by the Forest Nursery Station, Indian Head, Sask., by placing them to a depth of 2 feet 6 inches in a 5 per cent zinc chloride solution maintained at a temperature of 190° to 200° for half an hour to one hour. The solution was allowed to cool, and the posts were left standing in the solution for 36 hours. The posts absorbed 2 pounds to 3 $\frac{3}{4}$ pounds of solution, or 0.10 pound to 0.18 pound of zinc chloride. They were placed in service in the sprinkler line at the Nursery, together with a number of similarly treated posts, and remained in service four years, after which the three posts were removed and forwarded to these Laboratories, where one post was examined in detail and the other two visually.

Examination

Visual examination of the posts treated with zinc chloride was made by sectioning them at 10-inch intervals and spraying the freshly cut surfaces with potassium ferricyanide-potassium iodide-starch indicator solution, to show qualitatively the distribution and penetration of zinc chloride. A dark stain indicates the presence of zinc. Plates 1, 2 and 3 are reproductions of photographs of the sections of each post. Sections number 1, 2, 3, 4, etc., were at points 20 inches below the ground-line, 10 inches below the ground-line, at the ground-line 10 inches above the ground-line, and so on. It may be seen in Plates 1 and 2 that in sections above the ground-line, Nos. 4, 5, 6, 7 and 8, the preservative is not present at the circumference, while in Plate 3, showing Post No. 374, which was analysed in detail, it may be seen that in sections 4, 5, 6, 7, and 8, it is present near the circumference but not in the interior. In all posts heavier concentrations above the ground-line than below were indicated.

For the detailed analysis of Post No. 374, one-inch cross-sections were cut at 10-inch intervals, and analyses were carried out by standard methods for both zinc and chlorine. Results are given in Table 3 and shown graphically in Figure 1.

Table 3

Distribution of Zinc Chloride in a Butt-Treated
Post after 4 Years' Service

Position of 1-in. cross-section rel- ative to ground- line	Pounds of Zinc Chloride per cu. ft. calculated from:	
	Zinc Determinations	Chlorine Deter- minations
24 in. below	0.113	0.013
15 " "	0.143	0.024
5 " "	0.110	0.021
.5 " above	0.305	0.249
15 " "	0.255	0.257
25 " "	0.264	0.266
35 " "	0.225	-
45 " "	0.152	0.193
55 " "	0.155	0.170
Total zinc chloride in post	0.110 lb.	0.090 lb.

Discussion

An important conclusion to be drawn from a study of Table 4 and the supplementary graph, Fig. 1, is that service conditions effect not only a removal of water-soluble preservative from a standing post, but also a movement of the preservative to parts of the post, such as the centre above the ground, where preservation is relatively unnecessary. It is evident also that the zinc ion is more stable than the chloride ion, since the difference in concentrations above and below the ground-line is much greater for chloride than for zinc. The figures indicate that while zinc has moved upward in very appreciable quantities, chloride in more than equivalent quantities has either been lost from below the ground-line or has moved upward.

In conclusion, it may be mentioned that an examination in May, 1939, of the sprinkler line at Indian Head showed that the poplar posts treated with zinc chloride were only slightly decayed below the ground-line. Only one replacement in a total of sixty-four posts installed has been necessary in twelve years of service, and it appears that the small amount of zinc chloride remaining in the butts has increased the service life.

Summary

Movements of water in standing posts effect changes in the distribution of water-soluble preservatives, of which the most striking change is a movement of preservative to points above the ground-line. Under some

service conditions , at least, the preservative is not leached out of a post, but moves upward as noted. Again, as in the case of the ties examined in Section A, the indications are that a large percentage of the zinc chloride is removed in the first few years of service, and that the timber resists the attack of fungi for some time after a large percentage of the zinc chloride has been removed from the point requiring protection from decay.

C. Copper Sulphate Concentrations in Butt-treated Fence-posts after Treatment

What is known as the "blue-stoning" treatment for fence-posts has been used in Western Canada for many years. The green posts are placed upright, with the butts in a saturated solution of copper sulphate.

Materials Examined and History

Two aspen poplar posts were received from the Dominion Department of Agriculture and were described as having been treated at Nokomis, Sask., by steeping the butts in copper sulphate solution for 6 to 8 hours.

Examination

The posts treated with copper sulphate were sampled by cutting one-inch cross-sections commencing six inches from the butts and at 10-inch intervals thereafter. Freshly cut surfaces were daubed with potassium ferrocyanide to show penetration, and it appeared that most of the salt was concentrated in a quarter-inch outside shell extending nearly the full length of the pole in one case but less than half the length in the other. The analytical data shown in Table 4 verify this qualitative result.

Table 4

Distribution of Copper Sulphate in Butt- Treated Posts after Treatment (not sub- jected to service conditions)

<u>Distance of 1 in.</u> <u>cross-section from</u> <u>butt (inches)</u>	<u>Lb. of Copper Sulphate per cubic foot in:</u>		
	<u>Outer $\frac{1}{4}$ in.</u> <u>rings</u>	<u>Lightly Treated</u> <u>Area</u>	<u>Total Cross-</u> <u>section</u>
6 (Post No. 1)	1.45	0.22	0.36
16 "	1.23	6.15	0.28
26 "	1.44	0.18	0.32
36 "	1.06	0.16	0.25
46 "	1.00	0.13	0.21
56 "	0.97	0.07	0.17
66 "	0.84	0.01	0.13
76 "	0.62	Nil	0.09
6 (Post No. 2)	1.16	0.15	0.26
16 "	1.04	0.15	0.24
26 "	.71	0.08	0.13
36 "	.48	Nil	0.05

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Total amounts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per post	
No. 1	0.38 lb.
No. 2	0.13 lb.

Discussion

Regarding the examination of the posts treated with copper sulphate, the striking feature is the previously mentioned high concentration of preservative in a quarter-inch shell on the outside. The sapwood of each post was about two inches thick and no structural differences between the wood of the heavily treated zones and the adjacent sapwood could be detected; a ready explanation of the point is not apparent, unless it may be that the wood-water relationship in the treated green posts is somewhat the same as in the living tree.

- (1) Report on the Preservation of Wood--Gen. J.K. Barnes Surgeon-General, U.S.A., Gen. A.A. Humphreys, Chief of Engineers, U.S.A., Gen. M.C. Meigs, Quartermaster General, U.S.A., Gen. O.E. Babcock, Com'r. Public Buildings and Grounds to the Board of Public Works of the District of Columbia, with tabulated results of an examination of all the best known methods, conducted by Dr. B.F. Craig, A.A. Surgeon, U.S.A. and Dr. W.C. Tilden, A.A. Surgeon, U.S.A. at the Laboratory of the Surgeon-General's Office, Washington, D.C. 1872.
- (2) Bateman, E. The Leaching of Zinc Chloride from Treated Wood. Bull. Amer. Rly. Eng. Asscn. No. 227 (1920), pp. 73-87.
- (3) Harkom, J.F. Canada Lumberman, Jan. 15, 1931, p.24.



Plate 1. -- Cross-sections of Post No. 372



Plate 2. -- Cross-sections of Post No. 373

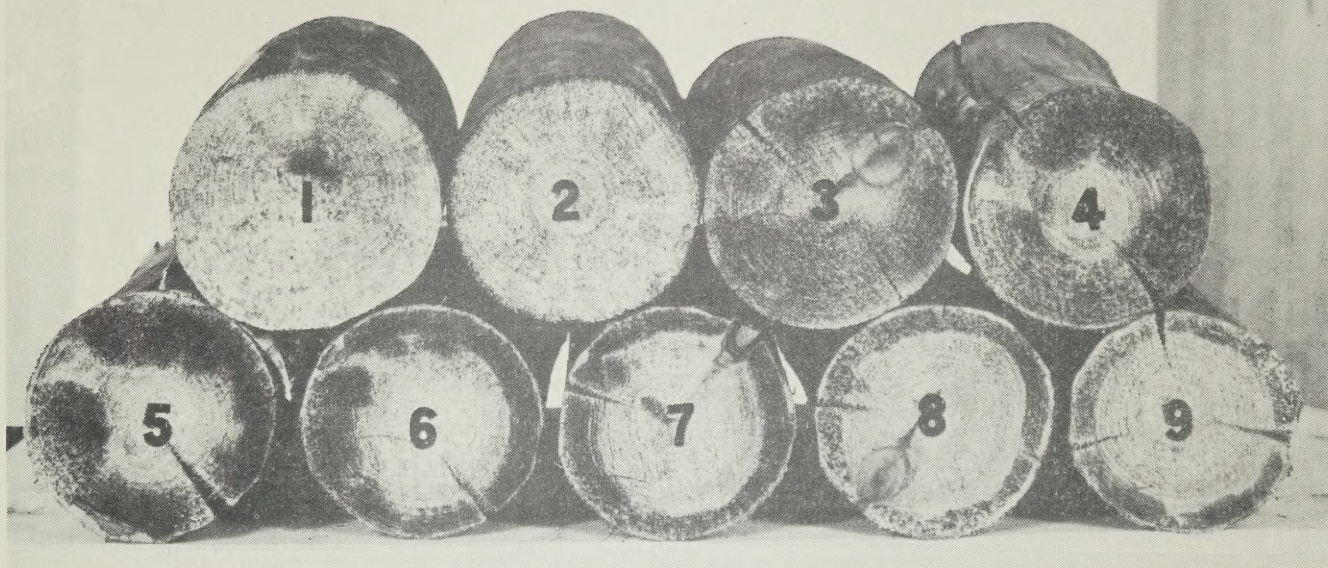


Plate 3. -- Cross-sections of Post No. 374

